The Effects of Ion-exchanged Cobalt Catalysts on the Gasification of Wood Chars in Carbon Dioxide

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Wood is composed primarily of cellulose, hemicelluloses, and lignin, with lesser quantities of extractives (material extractible in organic solvents) and mineral matter. The cottonwood species used in this study has been analyzed previously in this laboratory and it was found to contain 44% cellulose and 32% hemicelluloses on an extractive-free basis (1). The major component of the hemicelluloses is O-acetyl-4-O-methylglucuronoxylan, a polymer comprised of repeating units of xylose with acetyl and 4-O-methylglucuronic acid substituents substituted along the polymer chain. Figure 1 shows a representative chemical structure of this polymer, but does not correctly represent the frequency of substituents; approximately half of the xylose residues contain an acetyl group and there is one 4-O-methylglucuronic acid group per 10-20 xylose residues (1,2). These acid groups provide a means of incorporating catalysts into wood in a reproducible, highly-dispersed manner by ion exchange. Similar methods are used in catalysis of low-rank coals, but the ion exchange capacity of wood is much lower than that of coals. Our wood sample was found to contain 8-10 meq of carboxylic acid groups per 100 grams of wood (2), while low-rank coals typically contain 10-50 times higher concentrations of carboxylic acid groups (3,4).

The effects of several ion-exchanged catalysts on gasification of wood chars in carbon dioxide were described in an earlier paper (5). Ion-exchanged cobalt and calcium were found to be very effective catalysts of gasification of wood chars (HTT 800°C). In this paper we focus on the activity of cobalt catalysts for gasification of wood chars prepared at different heat treatment temperatures.

The gases formed by pyrolysis of low-temperature chars have also been determined by temperature-programmed desorption (TPD) using mass spectrometry. This analysis is indicative of structural features of the char and helps to elucidate the chemical transformations occurring in low-temperature chars (HTT 400°C) as they are heated to high temperatures.

EXPERIMENTAL

The wood sample used in this study was sapwood from black cottonwood (Populus trichocarpa). The wood was ground in a Wiley mill, sieved, and the 20/30 mesh fraction was retained for analysis. Chars were prepared in a tube furnace purged with flowing nitrogen, as described previously (1), and they were stored in nitrogen- or argon-purged containers between analyses.

Acid washing and cobalt ion exchange treatments were carried out by column percolation. For cobalt ion exchange the ground, acid-washed wood (2.5 g) was degassed in a small quantity of 0.01 M cobalt acetate solution and transferred to a glass chromatography column. The wood was then washed slowly with 500 ml of the 0.01 M cobalt acetate solution, followed by a thorough wash with distilled, deionized water to remove any unbound salt. Acid washing was carried out by essentially the same procedure except that 0.01 M HCl was used.

Reactivity measurements were carried out in a gasification reactor/detector system described previously (1). Briefly, the system consists of a small-scale temperature-programmed alumina reactor coupled to a combustible gas detector. The reactor can be maintained under either an inert or a reactive atmosphere. For inert conditions it is swept with nitrogen or helium (40 cc/min) and an equivalent flow of carbon dioxide is valved into the reactor for gasification.

The detector consists of a ZrO_2 solid electrolyte oxygen sensor which is maintained at a temperature of 650-700°C. Combustible gases formed in the reactor combine with an air stream after they leave the reactor and they undergo combustion in the hot detector. The detector monitors the depletion of oxygen content in the combined gas streams. The rate of carbon gasification is calculated from the combined gas flow rates and the oxygen depletion, assuming that one mole of carbon is gasified for each mole of oxygen consumed.

The rate of gasification of a char (HTT 800°C) prepared from untreated cottonwood is shown in Figure 2. The detector output can be integrated over the entire run to give the total extent of gasification, or it can be integrated above the baseline defined by the rate of pyrolytic gasification (dotted line) to give the extent of gasification due to reaction with CO_2. The extents of gasification reported in this paper are those due to gasification alone, i.e. excluding pyrolysis. Extents of conversion determined in this way compare well with measured weight losses, generally amounting to 100-110% of the weight loss. This system is preferred to gravimetric systems for our purposes because of its greater sensitivity and better control of temperature and gas flows.

The gasification system was modified to include a unit resolution mass spectrometer (Hewlett-Packard Model 5970B) for qualitative analysis of gas mixtures formed during pyrolysis of the sample prior to gasification. When the mass spectrometer was in use helium was used as the reactor purge gas. A splitter was placed in the gas line between the reactor outlet and the combustion air inlet. One meter of uncoated vitreous silica capillary tubing (0.20 mm ID) connected the splitter to the mass spectrometer. The capillary tubing was contained in a transfer line heated to 100°C. This arrangement diverted approximately 0.1 ml/min (0.3%) of the reactor gas flow to the mass spectrometer. On the basis of preliminary runs which revealed no high molecular weight pyrolysis products, the mass range of 10 to 110 amu was scanned and approximately fifteen mass spectra were accumulated per minute.

X-ray diffraction patterns were obtained using a Phillips diffractometer (CuKα, 35kV, 20mA) at a scan rate of 1 degree per minute. The sample was mounted on a glass slide using a vaseline smear.

RESULTS

Gasification Rate Determination

Table 1 shows the yields and reactivities of chars prepared at different HTT's from wood treated by ion exchange with cobalt, calcium, and potassium. The char prepared from one of the cobalt-exchanged samples was initially so reactive that the rate of gasification exceeded the detection limits of the detector, i.e., all of the oxygen in the combustion air supply was consumed by combustion of product gases. In this case the maximum rate of gasification was not observable, and the extent of gasification was therefore indicated as being "greater than" the value of the integrated detector response. The change in sample weight is indicated to show the total extent of reaction.

The reactivities of the chars containing cobalt catalyst are clearly less dependent on HTT than are those of the chars containing calcium and potassium. The reactivities of the latter chars toward gasification at 800°C increase by at least a factor of two as the HTT is reduced from 1000° to 800°C. This behavior is typical of trends shown by other investigators who have studied the effects of HTT on catalyzed gasification of lignite chars (6-8). By contrast, chars prepared from cobalt-exchanged wood at 800° and 1000°C are gasified to a similar extent at 800°C. When HTT and gasification temperature are reduced to 600°C, the char prepared from cobalt-treated wood is completely gasified, whereas the chars prepared from calcuim and potassium-exchange wood are completely unreactive at this temperature. When

cobalt-exchanged wood was charred and gasified at 400°C, no gasification occurred.

Table 1. Effect of HTT on extent of CO_2 gasification of chars from ion-exchanged wood. Gasification was for 30 min in 90.9 kPa of CO_2.

Treatement	HTT (°C)	Char Yield[b] (%, d.a.f.)	Gasification Temperature (°C)	Percent Gasified
Co-exchanged	1000	7.4	800	>69[a]
	800	9.2	800	73
			600	46
	600	12.9	600	96
	400	21.3	400	0
K-exchanged	1000	9.9	800	6%
	800	13.4	800	13
	600	17.5	600	0
Ca-exchanged	1000	8.1	800	36
	800	9.3	800	102[c]
	600	12.7	600	0

[a]Measured weight loss was 73%.

[b]Char yields are reported on a dry, ash-free basis assuming that the weight of the ash in the original wood remains in the char.

[c]Sample gasified completely. Percent of conversion determined by integration of combustible gas detector signal was consistently 100-110% of measured weight loss.

In order to better assess the dependence of reactivity on HTT in more detail, chars prepared from cobalt-exchanged wood at 100°C increments of HTT were gasified at 500°C. The results are shown in Table 2. The maximum reactivity is attained at the HTT 600°C. The reactivity decreases slightly when the HTT is raised to 700°C and more dramatically when the HTT is raised to 800°C. There is very little reaction for the sample of HTT 500°C. These results suggest that there is a threshold temperature for activation of the catalyst at about 600°C.

Table 2. Effect of heat treatment temperature (HTT) on the yield and reactivity of chars prepared from cobalt-exchanged wood. Gasification was carried out for 30 min at 500°C in 90.9 kPa of CO_2.

Sample	HTT	Char Yield (%, d.a.f.)	Percent Gasified
Co-exchanged wood	800	9.2	16
(0.23% Co, 0.34% ash)	700	10.9	66
	600	12.9	70
	500	17.2	3

To obtain a more detailed description of the nature of catalysis by cobalt it is helpful to consider the changes in reaction rate with extent of gasification or "gasification rate profiles", as shown in Figure 3. The gasification rate profile for the HTT 800°C char prepared from cobalt-exchanged wood undergoes two phases of reaction when gasified at 800°C. The first stage is very rapid but decreases as the

reaction proceeds. The second phase is characterized by a lower, more constant rate of reaction.

Figure 4 shows the gasification rate profile of a low-temperature char (HTT 600°C) gasified at 600°C. This char was much more reactive than the char prepared at 800°C and the maximum rate exceeded the detector capacity. As shown by the extents of gasification in Table 1, the low-temperature char was completely gasified in this case, and there was no evidence of the second, slower phase of gasification which was observed in gasification of higher temperature chars (HTT 800°C) at 800°C.

Pyrolytic Gasification of Low-Temperature Chars

We investigated the pyrolytic transformations that occur in chars (HTT 400°C) prepared from untreated and cobalt-exchanged cottonwood upon heating to 800°C in order to determine the existence and nature of any significant catalyst/substrate interactions which occur during pyrolysis. Figure 5 shows the gasification rate profile and the total ion profile for a char (HTT 400°C) prepared from untreated cottonwood heated in flowing helium to 800°C; both curves are from the same experiment. The shape of the gasification rate profile is distinctly different from that of the total ion profile. The former peaks at 10.5 min, corresponding to the end of the temperature ramp, while the total ion profile peaks at 8.5 minutes (600°C). The difference in the two profiles is apparently due to evolution of molecular hydrogen in the higher temperature range. Hydrogen is not detected by the mass spectrometer, but the combustible gas detector is very sensitive to the evolution of hydrogen, since its combustion requires three times more oxygen per unit weight than does combustion of carbon. Comparison of these curves therefore suggests that evolution of molecular hydrogen from the char predominates at high temperatures (T>650°C), while carbonaceous compounds are evolved at lower temperatures.

Analysis of individual mass spectra acquired during these experiments indicates that the most prominent species evolved are CO (m/z 28) and CO_2 (m/z 44), with CO_2 evolution decreasing at higher temperatures. There is also a smaller, but significant quantity of water (m/z 18) evolved throughout the pyrolysis process. Mass peaks indicative of methanol, low molecular weight aldehydes and hydrocarbons are also present in very low abundances.

The gasification rate profile shown in Figure 5 has been demonstrated to be representative of untreated wood as well as wood treated with alkali and alkaline earth metals (9). However, as shown in Figure 6, the gasification rate profile of low-temperature chars containing the cobalt catalyst differs from this pattern. The profile for the char (HTT 400°C) prepared from cobalt-exchanged wood peaks much earlier than that of the char from untreated wood, and this appears to be due to a peak (5.8 min, 630°C) superimposed on the profile of the untreated wood. The same peak is evident on the total ion profile, which suggests that this additional transition involves evolution of carbonaceous species. However, analysis of the mass spectra corresponding to this peak does not indicate that this peak in the gasification rate profile corresponds to the enhanced evolution of any single product. The data do not, therefore suggest a specific solid phase reaction involving interaction of the cobalt catalyst with carbon. However, we believe that this transition, which is unique among the catalysts studied and corresponds to the HTT at which the catalyst became active (see Tables 1 and 2), corresponds to the reduction of the catalyst to the elemental state which has been shown to be the active state of transition metal catalysts for gasification of graphite (10), wood chars (11), and coal chars (12).

X-Ray Diffraction

X-ray diffraction (XRD) patterns for chars prepared at 800° and 1000°C from cobalt-exchanged wood are shown in Figure 7. The diffraction patterns show evidence

of different crystalline phases in the two chars. Two of the peaks in the diffraction pattern of the higher temperature char, correspond to d-spacings characteristic of elemental cobalt (2θ=44.2° and 51.5°) (13). The large, broad peak in the XRD pattern for this char is not identified and probably corresponds to ordered regions in the carbon lattice. The peaks in the diffraction pattern of the char of HTT 800°C could not be correlated with a crystalline cobalt compound or with compounds of the small quantity of calcium remaining in this sample. No XRD peaks were observed in chars (HTT 800°C) from potassium- or calcium-exchanged samples.

DISCUSSION

The results obtained in this study demonstrate the exceptionally high activity of cobalt in catalyzing the gasification of wood chars in carbon dioxide. A pyrolysis temperature of about 600°C appears to be required to activate the catalyst. At higher heat treatment temperatures the maximum catalytic activity declines.

Figueiredo et al. studied the gasification of chars (HTT 850°C) prepared from pine wood doped with higher levels of cobalt nitrate (1.6% metal) (14). These authors report gasification behavior in pure CO_2 similar to that reported here, i.e., an initial period of rapid gasification lasting a few minutes followed by slow gasification of the remaining char. They measured gasification rates in the temperature range of 740-910°C and report an initial (presumably maximum) rate at 805°C of 0.18 min^{-1} which is very comparable to the initial rate of 18 mMoles $C \cdot min^{-1} \cdot g^{-1}$ (0.22 $g \cdot g^{-1} \cdot min^{-1}$) found in this study for a char (HTT 800°C) gasified at 800°C (see Figure 3). Their data extrapolate to much lower rates at 600° and 500°C than those found in this study for gasification of a char prepared at 600°C (see Figure 4). The effect of the higher concentration of cobalt in their wood is presumably offset by lower dispersion of the catalyst due to the mode of addition, higher HTT, and larger heat treatment time used in preparation of chars (1 hr vs 10 min in this study). These authors suggest that the decline in activity is due to oxidation of the active reduced form to CoO during gasification, and they cite XRD evidence for CoO in chars after gasification. However, the results of this study show that the rapid, catalyzed stage of gasification can be maintained throughout the reaction to give complete gasification of chars prepared and gasified at lower temperatures (600°C, see Figure 4). We therefore believe that the slower stage of gasification is due to gasification of carbon which is no longer in contact with the catalyst due to its agglomeration at high temperatures.

The combined data from this study suggest a picture of catalysis by cobalt involving (1) reduction to an active catalytic state, probably elemental cobalt, near 600°C followed by (2) agglomeration of the catalyst particles to form crystalline cobalt. The latter process, which is much more important at temperatures greater than 800°C, gives rise to two distinct phases of gasification. The first, corresponding to gasification of carbon in contact with cobalt crystallites is fast, while the second, slower rate corresponds to gasification of char which is not in contact with catalyst (see Figure 1). On the basis of the XRD evidence for crystalline elemental cobalt in chars of HTT 1000°C, we believe that elemental cobalt is the active phase of the catalyst throughout the reaction, but it is detectable by XRD only when crystallite growth is at an advanced stage.

The presence of reduced cobalt in wood chars also suggests that the relative activities of transition metal catalysts in gasification by carbon dioxide might be associated with the rate of dissociation of the reactant gas on the metal surface. Grabke has reported rate constants for dissociation of CO_2 on cobalt, nickel and copper at 1000°C (15), which are pertinent to the non-equilibrium conditions used in our studies. The rate constants decrease in the order: $k_{Co} > k_{Ni} >> k_{Cu}$, which is the same order of relative activities reported for transition metal catalysts in the earlier paper (5). The results of these studies are therefore consistent with an oxygen transfer mechanism, as described by Walker et al. in the iron-catalyzed

gasification of graphite by CO_2 (10) or possibly an oxygen 'spillover' mechanism (16), depending on whether the adsorbed atomic oxygen reacts with the metal to form the metal oxide before reacting with carbon in contact with the catalyst particle.

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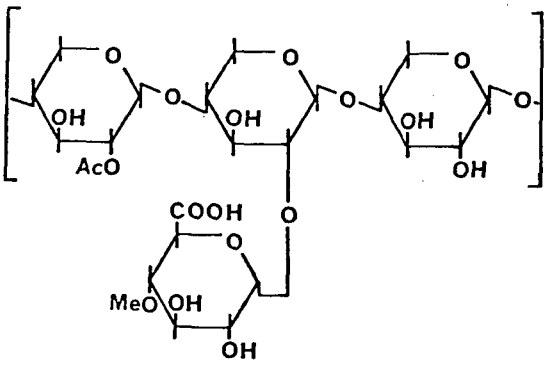

Figure 1. Representative structural elements of acetyl 4-O-methylglucuronoxylan.

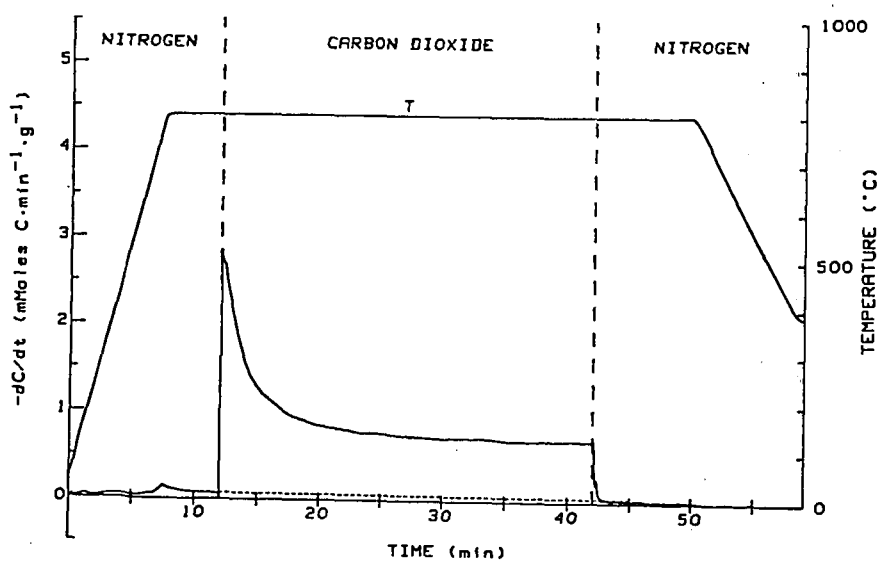

Figure 2. Gasification rate profile for gasification at 800°C of char (HTT 800°C) prepared from untreated cottonwood.

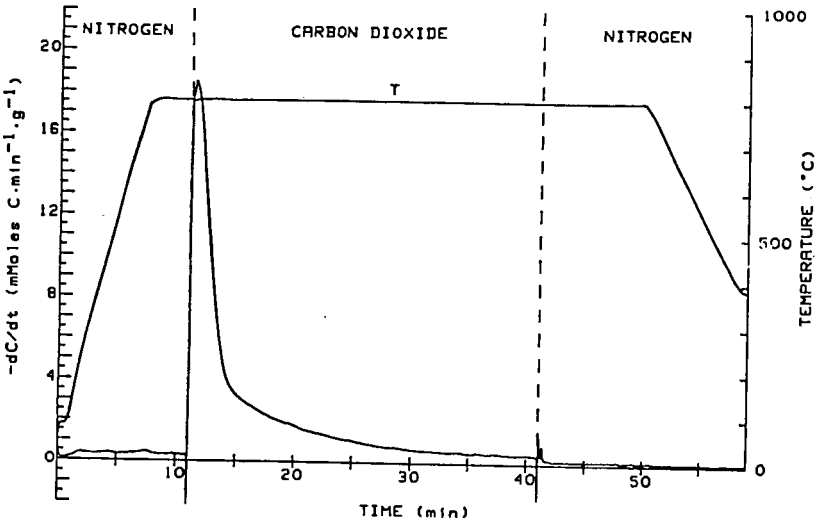

Figure 3. Gasification rate profile for gasification at 800°C of char (HTT 800°C) prepared from cobalt-exchanged cottonwood.

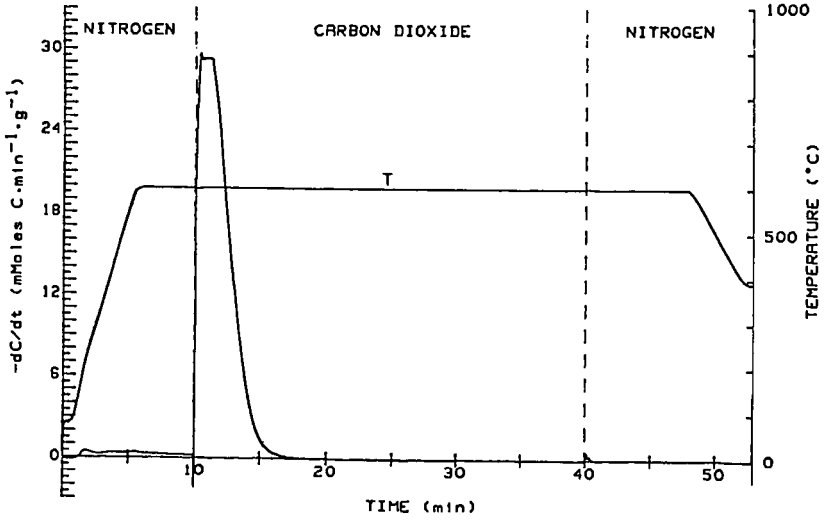

Figure 4. Gasification rate profile for gasification at 600°C of char (HTT 600°C) prepared from cobalt-exchanged cottonwood.

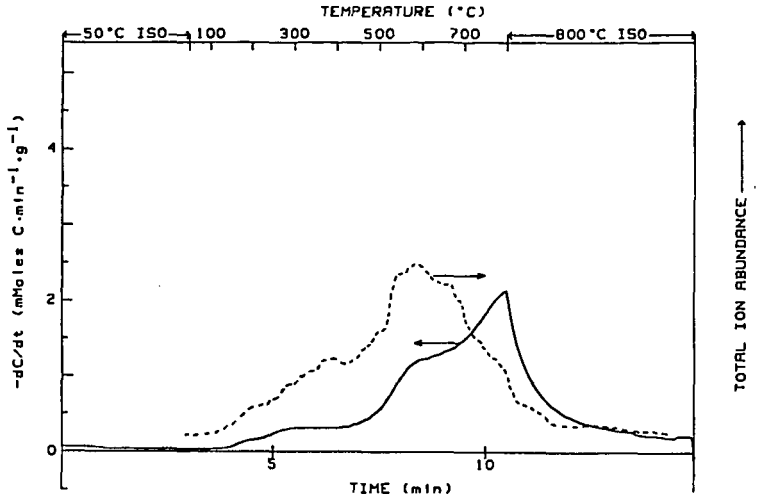

Figure 5. Gasification rate profile and total ion profile for pyrolytic gasification in helium of char (HTT 400°C) prepared from untreated cottonwood.

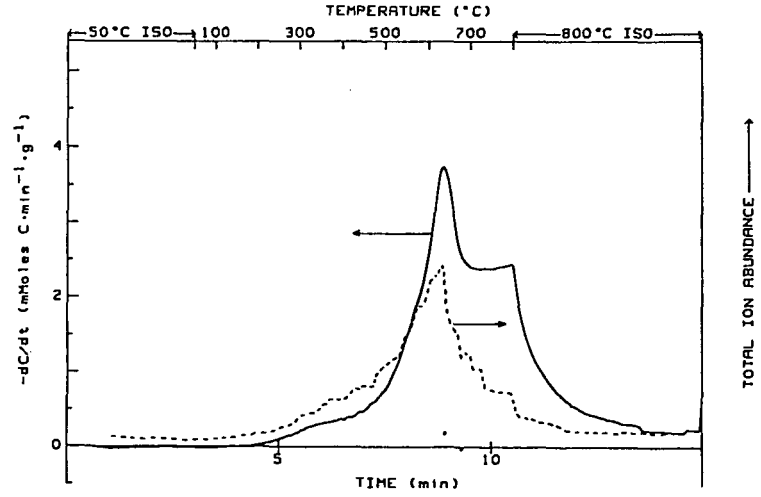

Figure 6. Gasification rate profile and total ion profile for pyrolytic gasification in helium of char (HTT 400°C) prepared from cobalt-exchanged cottonwood.

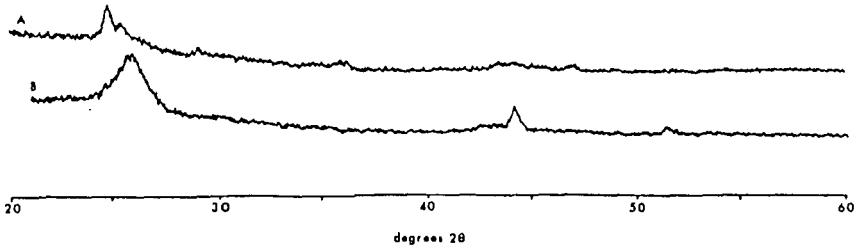

Figure 7. XRD patterns obtained from chars prepared from cobalt-exchanged cottonwood at HTT's of (A) 800°C and (B) 1000°C.